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PART B. WORKING PAPERS: AN HISTORICAL SURVEY OF THE DEVELOPMENT OF HERBICIDES

NATIONAL ACADEMY OF SCIENCES-NATIONAL RESEARCH COUNCIL

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An Historical Survey of the Development of Herbicides

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A weed is best defined as a plant out of place in the pattern of man's existence. As a nomad and hunter, man discerned only good plants that were edible or useful and bad plants that were not. When he first settled down to cultivate plants some ten thousand years ago, he must slowly have become aware of the damage caused by weeds. The first effective tool man devised to get rid of unwanted vegetation was the hoe. Very slowly this tool was supplemented by primitive plows drawn by domesticated animals, and, with time, primitive harrows were added. These means of cultivation, combined with hand weeding, remained substantially unchanged for thousands of years. Indeed, no major advance took place until the eighteenth century invention of the moldboard plow, which inverted the top layer of soil and buried the weeds.

THE INITIAL DISCOVERIES AND THEIR EXPLOITATION

The genesis of an entirely new approach to the control of weeds came in 1896, when a French viticulturist named Bonnet observed while spraying his vines with Bordeaux mixture, a newly discovered fungicide, that seedlings of *Sinapis arvensis* L. (wild mustard), one of the commonest weeds of western Europe, were killed when they were wetted by the spray. Subsequently, he showed that one of the ingredients of Bordeaux mixture, namely copper sulfate, could kill selectively the wild mustard growing in a cereal crop. The significance of this discovery did not immediately attract the attention of scientists; consequently, no guidelines were developed and the approach remained empirical. In Europe, test compounds were selected which were cheap and readily available. It was known that when plant cells are placed

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in strong solutions of water-soluble compounds, water is extracted from the tissues and disruption and death follow. So either concentrated solutions or the powdered materials were applied to the weed-infested crops. Most attention was given to cereals, since it was likely that the leaves of weeds with broad horizontal surfaces would catch more of the spray or powder than the upright narrow leaves of the cereal. Widely-tested compounds included sodium nitrate and ferrous sulfate as sprays and kainit, a potassium-rich mineral, as a powder. Their performances were erratic. As with copper sulfate, their effectiveness depended upon a spell without rain after application. Moreover, an outright kill of a relatively few weed species was achievable and then only when they were seedlings.

In France in 1897, Duclos tried out dilute sulfuric acid for the control of weeds in cereals, but no recommendations were made until Rabate started to reinvestigate its possibilities in 1911. The first World War interrupted the studies, but subsequently Rabate went on to demonstrate that sulfuric acid at concentrations of 9-18 percent had many advantages over the other compounds so far tested. It killed a much wider range of annual weeds and its effectiveness was not impaired by rain if only a few hours of fine weather intervened.

In North America, contemporaneous developments were more concerned with problems of perennial rather than annual weeds. Jones in 1899 and James and Orton in 1909 demonstrated that sodium arsenite could be effectively employed for the elimination of vegetation on roads or industrial sites. In 1911, Wilcox found that dilute solutions could selectively control weeds in Hawaiian sugarcane. Because of the possible hazards to man and beast, interest was transferred to other, less toxic compounds. It was

already apparent by 1904 from work in Europe and America that chlorates and perchlorates were toxic to some plants, but it was not until later that sodium chlorate was employed in Europe to prevent the invasion of paths or tracks by perennials.

Between the two wars extensive tests were carried out in North America to determine the conditions that allowed sodium chlorate, either alone or mixed with other materials to reduce fire risk, to be employed against heavy infestations of bindweeds, thistles, or perennial grass weeds. Similar smaller-scale investigations in Europe reached the same conclusions: namely, that a good control of the more resistant weeds could be attained if heavy enough applications were made. However, there remained an aftermath of residual toxicity in the soil that would not allow normal production without a fallow period, although in grassland it was still possible to use lower concentrations to kill some of the more susceptible weeds without undue harm to the grasses.

Later, Blackman and Templeman at Jealotts Hill Research Station, which was established in England by Imperial Chemical Industries in 1927, undertook quantitative experiments. Their data, analyzed statistically to assess errors, reinforced the conclusions reached by Rabate. It was shown that effective kill of the individual weeds was dependent on adjusting the concentration of the acid to the stage of development. In addition, in the cereals themselves resistance to injury was maximal at certain stages of development. These experiments also brought out for the first time the importance of taking into account the physical properties of the spray solution. The addition of a wetting agent, which is compatible with highly acidic solutions, greatly improved

the kill of weeds with waxy leaves, since the spray droplets spread on the surfaces and were retained, instead of rolling off. This greater degree of retention was also observed in the crop, although to a lesser extent. So the advantages of adding a wetting agent had to be weighed against a possible greater check to the growth of the cereal.

Further analysis showed that following spraying the gain in yield of grain was dependent on the season, the quantity and nature of the dominant weed, and the level of inorganic nitrogen in the soil. Under some conditions the yield was more than doubled, in others it increased less than 10 percent. By 1932 Korsmo had published the results of his extensive investigation on the performances of the then-available herbicides for weed control in cereals in Norway. On the bases of no less than 211 field trials he found the average increase in grain production following weed suppression to be 25 percent.

The use of sulfuric acid was taken up enthusiastically by the larger farmers in Great Britain and France, who purchased the then-available spraying machines. The enthusiasm waned not because spraying was unsuccessful, but because the machines became inoperative due to corrosion and the traditional neglect of farm machinery which ruled at that time. In the United Kingdom it was not until 1940 that the properties of the newer corrosion resistant materials became appreciated and relatively farmer-proof machines were produced.

DEVELOPMENTS DURING WORLD WAR II

The need under the conditions of war to expand crop production and at the same time to conserve manpower was reflected in many countries in

more active programs of research, not only to develop existing methods of weed control but also to find new ones.

Nitro-phenols

In 1935 Truffaut and Pastac took out a patent in France on dinitro-ortho-cresol, a well established synthetic dyestuff, as a selective herbicide, and it was introduced into the United States in 1937. An active program of development was started in California using the sodium salt. But it was only during the war that modifications were made both to the formulation and the chemical structure by Crafts in California and by Blackman and others in England that demonstrated its wider potential for weed control in cereals and the extension of the use of selective herbicides to new crops such as peas, flax, and linseed.

Mineral Oils

It has long been known that discarded sump oil, if applied to the stump of a felled tree, will prevent resprouting. In California waste products from oil refineries were used to suppress weeds on roadsides and it was observed that species belonging to the Umbelliferae tended to take over. It is not known who made the deduction that some fractions of mineral oils might selectively kill weeds in umbelliferous crops, nor is it clear who started the initial experiments. However, during the course of wartime investigations in the United States, Australia, and Great Britain, it was established that light mineral oils of the right specification were excellent for weed control in carrots, parsnips, and celery. Later, it was found that this procedure was also applicable to forest nursery beds of many coniferous species.

Preemergence Spraying

In England in 1942 Blackman observed that when certain horticultural crops were sown the weeds emerged in advance of the crop. He concluded that a herbicide applied at the time of preemergence need not be selective if it was either rapidly destroyed at the soil surface or did not enter the crop via the soil. The application of this concept of preemergence spraying, using in the first instance dilute sulfuric acid, allowed a greatly increased acreage of crops such as onions or leeks to be grown, previously unfeasible because of the high labor requirement for hand weeding in the early seedling stage. Later, in 1945, Templeman and Sexton drew attention to the potential of aryl carbamic esters for selectively killing grass weeds in the germination phase. Since then the procedures have been refined to permit specific weeds to be suppressed before emergence in selected crops, for example, wild oats in cereals.

Development of Synthetic Hormones as Herbicides

During the 1930's the discovery of synthetic plant hormones excited wide interest both for the nature of their reactions and their commercial application. Imperial Chemical Industries was concerned with this field of development and Templeman examined the claim put forward by Canadian workers that treating oat seeds with napthylacetic acid, a synthetic hormone, accelerated their growth. In the course of his experiments he sprayed a whole series of young potted oat plants with increasing doses of the hormone and, just like Bonnet more than 40 years before, he noted that some chance seedlings of wild mustard were killed. Since the cost of the hormone and the quantity required per acre made it an uneconomical proposition, a search

was started for new synthetic hormones which were cheaper to make and more active. After "screening" many compounds in the laboratory and greenhouse the two most promising were (2,4-dichlorophenoxy)acetic acid and (2-methyl-4-chlorophenoxy)acetic acid, now known universally as 2,4-D and MCPA. This development was reported to the Agricultural Research Council in 1942.

Parallel to these studies, Thornton, Nutman, and Quastel in England were investigating at Rothamsted Experimental Station the mechanisms by which nitrogen-fixing bacteria in soil enter the root hairs of leguminous plants to form nodules. They demonstrated that entry was associated with the excretion of a hormone by the bacteria. At this point Quastel went to the United States where he visited the Boyce Thompson Research Institute, well known for its research on plant hormones. There he was shown the aberrant growth of tomato induced by very low doses of a new compound, namely 2,4-D. On Quastel's return to England this compound was compared with others for its effects on nodule initiation and the processes of germination of leguminous and non-leguminous species. It at once became apparent that the degree to which germination was disrupted was dependent on the plant species and on the relative resistance of chlorinated compounds to microbial breakdown in the soil. At this point the Agricultural Research Council was informed that 2,4-D might be a powerful new selective herbicide.

By this time a research team, headed by Blackman and sponsored by the Agricultural Research Council, was already investigating new methods and techniques of weed control and it was decided that to ensure rapid development the further testing of 2,4-D and MCPA in the field should be incorporated into the program. Accordingly, in the spring of 1943, an extensive comparative program was initiated covering a range of herbicides and crops. By the end

of 1943 it was clear that 2,4-D and MCPA had unique properties as herbicides and so according to the agreement made between Churchill and Roosevelt at the time of the fall of France, these discoveries were passed to the American government.

Studies were also under way in the United States. In 1941 E. J. Kraus, the head of the Department of Botany at the University of Chicago, became interested in the potential of synthetic hormones for crop destruction, and the results of the initial experiments were reported to a joint committee of the National Academy of Sciences and the National Research Council. Subsequently, in 1943, under an Army contract, laboratory experiments were conducted to evaluate the toxicity of 2,4-D and a related compound (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T) to rice. In 1944 the work was transferred to Fort Detrick, Md. after it had been decided to extend the program on biological warfare to include the effects of chemical agents on living plants. At the time of this transfer research had been started at the U.S. Department of Agriculture at Beltsville, Maryland by Mitchell, an associate of Kraus, and others to explore the value of 2,4-D and 2,4,5-T as selective herbicides.

The first field trials were started in the summer of 1944 by Hamner and Tukey at the Agricultural Research Station, Geneva, New York on the eradication of bindweed and by Mitchell and Marth at Beltsville on the control of dandelions in turf. The spectacular effects on bindweed were reported publicly in a preliminary article by Hamner and Tukey in December 1944. This caused great perturbation amongst the three groups of British workers, since under the Churchill-Roosevelt agreement publication was precluded until the war was over. As a consequence, accounts of the British

contribution were not released until 1945. It now seems quite clear that neither of these two groups knew anything about the British information nor the agreement about postwar publication.

The initial observations made by Hamner and Tukey that 2,4,5-T was superior to 2,4-D for the control of bindweed were followed up by testing the reactions of a wide range of perennials. It was found that many woody species were particularly susceptible and that spraying with 2,4,5-T, alone or mixed with 2,4-D, had many advantages for the eradication of scrub invading grassland or the suppression of vegetation beneath power lines in wooded country. It also showed promise in the management of forests or plantations where unwanted species could be killed by applying to the base of the trunk esters of 2,4,5-T mixed with mineral oils to aid penetration.

POSTWAR DEVELOPMENTS

Low Volume Applications

In the next five years there were further important developments. For many herbicides maximal control is not feasible unless the shoots of the weeds are covered by a thin film of spray solution, because only the tissues in contact with the solution are killed. This limitation does not apply to the substituted phenoxyacetic acids, since once they enter the shoot they can move freely within the plant. Consequently, a few discrete drops of a higher concentration can be equally effective as a continuous film. The possibility of minimizing the quantity of spray solution applied per acre was first exploited on the Canadian prairies where low rainfall restricts the availability of water in areas of grain production. Here the introduction of

specially designed low-volume sprayers and formulations of 2,4-D which permitted high concentrations to be used established that as little as 10-15 gal could be substituted for the traditional 50 or more gal/acre. As a consequence, low-volume spraying was widely adopted in the grain belt and subsequently in many other semiarid regions where a large volume per acre would be impossible. It also pointed the way to the feasibility of aerial applications.

Changes in Cultural Practice

In some crops, the increased efficiency of herbicides permitted both elimination of mechanical hoeing between the rows and adjustment of crop spacing and density for better production. These procedures met with notable success. In the Corn Belt the traditional pattern was to sow a few seeds of corn in clumps (hills) on the square, so as to allow inter-row cultivation both across and along the rows. Without this requirement the width between the rows could be reduced and the seeds evenly spaced along the row, thereby reducing competition between corn plants and allowing the potential of yield to be raised as a consequence of a more uniform plant cover. Again, in Europe the advantages of narrowing the distance between the rows of carrots not only markedly increased the yield but also dispensed with the need for thinning the crop.

New Compounds

These many developments greatly stimulated research and development by agricultural research stations, the universities, and industry. Many programs were established to search for new compounds or to find further applications. In the early fifties these programs were coming to fruition

with the announcement of novel compound types, including many which are now firmly established. The three years 1950-1953 saw the development in the United States of (1) chlorinated benzoic acids following the investigations of Minarik and others at Fort Detrick; (2) halogenated aliphatic acids, including dalapon by research workers at the Dow Chemical Company; (3) substituted ureas of which the first to be developed by the Du Pont Company was monuron; and (4) amitrol, first investigated for the defoliation of cotton prior to mechanical plucking at the Texas Agricultural Experimental Station in 1952.

By 1955 Wain and his co-workers in England had established that some species but not others were capable of converting 4-(MCPB) and 4-(2,4-DB) compounds with a low level of phytotoxicity, into MCPA and 2,4-D, with their highly toxic properties. A knowledge of the differences between species in their capacity to break down these two compounds would allow prediction of selectivity. For example, in Great Britain weeds were controlled in cereal crops undersown with legumes. Another chemically-allied group of compounds, the substituted phenoxypropionic acids, was developed in the United States by the Dow Chemical Company for the eradication of woody species (fenoprop), and mecoprop was created by the Boots Pure Drug Company in England for the eradication of some annual weeds which are resistant to 2,4-D and MCPA.

By 1960 Geigy Agricultural Chemicals in Switzerland had established the value of the triazine group of herbicides not only for the selective control of weeds in corn and other crops (initially simazine) but also for non-selective control at sites where there is a requirement for bare ground. Contemporaneously, Imperial Chemical Industries in England had discovered

two bipyridylium quaternary ammonium salts, which they named diquat and paraquat. These compounds killed very rapidly the aerial parts of a wide range of dicotyledenous and monocotyledenous species but their immobilization in the soil resulted in little residual effect. These characteristics have led on to further studies of "chemical plowing," that is the sowing of crops into land which has not been previously plowed but where the weed seedlings have first been killed by spraying.

By 1960 the guidelines had been established for the developments which have taken place up to the present day. Within each of the broad groups of herbicides further compounds have been synthesized and examined for their potential as herbicides and a number of new compounds found to fill in the gaps. In 1950 there were 31 commonly-used herbicides in the United States. By 1960 the number of recognized herbicides, excluding formulations, had reached 67 and by 1972, more than 125 were listed for the control of weeds in crops, grassland, woodland, and waterways. There has also been a progressive widening of interest in the use of herbicides in tropical and subtropical countries, which started soon after the end of World War II with field trials of 2,4-D, MCPA, and 2,4,5-T.

In conclusion, it should be emphasized that along with all the field investigations of an applied nature, much basic research has been done to unravel the principles of selectivity and the nature of herbicidal action. The problems have proved to be exceedingly complex. Indeed, only for some simple inorganic compounds, such as sulfuric acid, can the factors involved be defined with precision. For the remainder, the primary pathways determining the toxicity of the principal groups of herbicides have been delineated

but the more subtle differences controlling the selective action in many cases remain unresolved. This does not imply that during the course of these studies the frontiers of knowledge have not been pushed back on a range of fronts. As a consequence more critical programs of research on herbicides can be planned as new concepts arise. One example is given by way of illustration. By 1965, studies of the mechanisms by which synthetic hormones control defoliation had established the role played by ethylene in determining the abcission of leaves. In seemingly an entirely different field, the Rubber Research Institute of Malaya in conjunction with British workers has for many years been examining the ability of synthetic hormones, such as 2,4,5-T, and other chemically unrelated compounds to increase the production of latex when applied to the trunks of rubber trees. In 1966 it was postulated that a common feature of these disparate compounds was the production of ethylene in the tissues and as a follow-up it has now been shown that under some conditions a 50 percent increase in the yield of rubber is attainable by the application of compounds which generate ethylene within the tree.

There is no doubt that in the future this cross-fertilization of ideas and concepts will lead not only to further advances in the chemical control of weeds but to entirely new ways of increasing productivity.

REFERENCES

Abraham, P.D., W.J. Blencoe, S.E. Chua, J.B. Gomez, G.F.J. Moir, G.W. Pakianathan, B.C. Sekhar, W.A. Southon, and P.R. Wycherley. 1971. Novel stimulants and procedures in the exploitation of *Hevea*. I. Introductory review. *J. Rubber Res. Inst. Malaya* 23:85-89.

Audus, L.J. 1964. Physiology and biochemistry of herbicides. Academic Press, London and New York. 555 pp.

Blackman, G.E. 1945. Recent developments in chemical methods for the selective control of weeds. *J. Roy. Agric. Soc. England* 106:137-49.

Blackman, G.E. 1945. A comparison of certain plant growth regulators with other selective herbicides. *Nature* 155:500-1.

Fryer, J.D. and S.A. Evans. 1970. Weed control handbook. Vol. 1: Principles, 5th ed. Blackwell Scientific, Oxford. 494 pp.

Nutman, P.S., H.G. Thornton, and J.H. Quastel. 1945. The inhibition of plant growth by 2,4-dichlorophenoxyacetic acid and other plant growth substances. *Nature* 155:498-500.

Peterson, G.E. 1967. The discovery and development of 2,4-D. *Agric. History* 41:243-53.

Robbins, W.W., A.S. Crafts, and R.W. Raynor. 1952. Weed control: a text book and manual, 2nd ed. McGraw-Hill, London. 503 pp.

Roberts, H.A., and G.E. Blackman. 1950. Studies in selective weed control. III. The control of annual weeds in leguminous crops with 2,4-dinitro-6-secondary-butyl-phenol. *J. Agric. Sci.* 40:263-74.

Slade, R.E., W.G. Templeman, and W.A. Sexton. 1945. Differential effects of plant growth substances on plant species. *Nature* 155:497-8.

Templeman, W.G. and W.A. Sexton. 1945. Effect of some aryl carbamic esters and related compounds upon cereals and other plant species. *Nature* 155:630.

U.S. Congress House, Committee on Science and Astronautics, Report to the Sub-Committee on Sciences, Research, and Development. 1969. A technology assessment of the Vietnam defoliant matter: a case history. Science Policy Research Division, Legislative Reference Service, Library of Congress, Government Printing Office. 73 pp.